Dyes and Pigments, Vol. 29, No. 1, pp. 1–21, 1995

0143-7208/95 $9.50 + 0.00

0143-7208(95)00026-7

Design and Properties of Reactive Dyes with Heterobifunctional Reactive Systems

Takashi Omura,* Kazufumi Yokogawa, Yutaka Kayane† & Yasuo Tezuka†

Fine Chemicals Research Laboratory, Sumitomo Chemical Co., Ltd,
1-98, 3-chome, Kasugade-naka, Konohana-ku, Osaka 554, Japan

(Received 16 January 1995; accepted 22 February 1995)

ABSTRACT

Dyes with two different reactive groups have been investigated for establishing the molecular design concept of heterobifunctional reactive dyes. The β-sulphatoethylsulphonyl/monochlorotriazinyl combined reactive system on the same side of a chromogen offers great flexibility in molecular engineering techniques for the dyes, making it possible to achieve improved application properties. The bridge links between the two reactive groups and between the chromogen and the triazine play a vital role in optimizing the system. Thus, the heterobifunctional dyes with a 4-chloro-6-[3-(β-sulphatoethylsulphonyl)anilino]-1,3,5-triazin-2-ylamino group show the best overall picture with respect to application properties, permitting the conclusion that their distinct advantages over comparable mono- and homobifunctional dyes can be achieved by cooperative functions of these structural units.

1 INTRODUCTION

In the interest of understanding the role of bifunctionality in modifying the application properties of reactive dyes for cellulose, we have investigated a series of reactive dyes in which the chemical structures of bifunctional reactive systems are varied in a systematic fashion. Bifunctionality built into dyes has been suggested to be technically important for improving their application properties.[1] For example, the heterobifunctional CI

---

* To whom correspondence should be addressed.

† Present address: Osaka Works, Sumitomo Chemical Co., Ltd, 1-98, 3-chome, Kasugade-naka, Konohana-nu, Osaka 554, Japan.

TABLE 1

Possible Application Properties of VS/MCT Bifunctional Reactive Dyes, and Comparable VS and MCT Monofunctional Reactive Dyes

Reactive dyes	*Dyeing properties*				*Fastness properties*		
	Temperature sensitivity	*Exhaustion ability*	*Levelness and reproducibility*	*Washing-off*	*Light and perspiration–light*	*Chlorinated water*	*Acid/alkaline hydrolysis*
VS/MCT bifunctional	mild	O	O	O	Δ–O	O	O/O
VS monofunctional	sensitive	Δ	Δ	O	Δ	x–Δ	O/Δ
MCT monofunctional	sensitive	Δ–O	Δ	Δ	Δ–O	Δ–O	Δ/O

O: Good, Δ: Fair, x: Poor.

Reactive Red 240, having a VS (vinylsulphonyl or its precursor) and an MCT (monochlorotriazinyl) group, offers distinct advantages over structurally similar monofunctional dyes having either one of these groups; a lower sensitivity to changes in dyeing conditions is the most characteristic feature. In contrast, the homobifunctional CI Reactive Black 5 and CI Reactive Red 120 with two VS and two MCT groups, respectively, do not show this feature. In previous studies,[1-4] developments of bifunctional dyes were carried out specifically to exploit the possible advantages accruing from the presence of two reactive groups.

The question remains as to what type of bifunctional dye creates such advantages. Whilst the dye can react twice with cellulose, leading to the possibility of high fixation, the lower sensitivity to changes in dyeing conditions is not fully understood. These features may be explained partly by the bifunctionality, but it should be noted that this factor alone does not fully answer the question, because diffusibility and substantivity must also influence the dyeing behaviour.[5] Moreover, the fastness properties of the dye, which may be fixed to cellulose with different types of fixation mode, are not fully understood from a chemical point of view.

The present investigation addresses the important questions concerning heterobifunctional dyes. Firstly, how molecular design can be used to reveal such advantages, and in particular, whether it can then offer a rational approach to the design of industrially useful dyes. Secondly, whether such dyes are sufficiently resistant to various conditions, and in particular, how the different types of fixation mode affect their fastness properties. To answer these questions, we have designed and synthesized a series of heterobifunctional dyes, and examined their structure–property relationships.

Important features pertaining to the application properties for the optimized VS/MCT bifunctional reactive dyes, and those for comparable VS and MCT monofunctional reactive dyes, are summarized in Table 1.

2 RESULTS AND DISCUSSION

2.1 Selection of reactive groups and their positioning

The first stage of the design process for heterobifunctional dyes involved the selection of two reactive groups and their linkage to a chromogenic system. These are important considerations when designing the dyes, since a reactive system always plays a significant role in modifying dye application properties. Figure 1 shows the schematic chemical structures of a designed VS/MCT dye (**I**), its counterpart dye (**II**) and their comparable dyes (**III** and **IV**). In **I**, which can be designated as an 'unseparated'

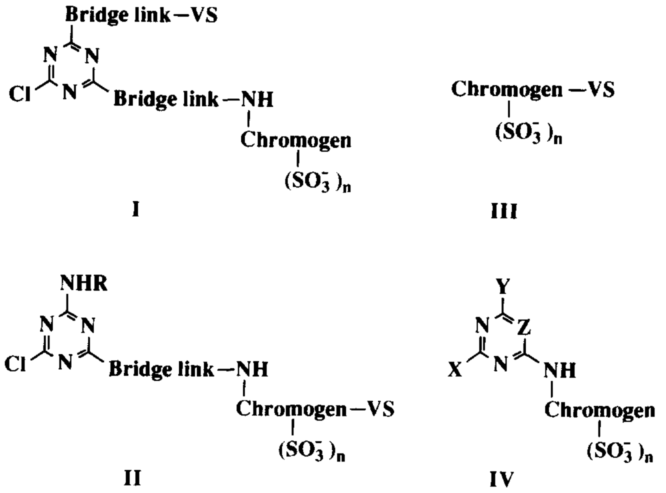


Fig. 1. Schematic chemical structures of VS/MCT dye (**I**) designed as the most rational skeleton of heterobifunctional dyes and of comparable dyes: its counterpart dye (**II**), VS dye (**III**) and *N*-heterocyclic reactive dye (**IV**). *VS* is vinylsulphonyl or its precursor. *R* is a nonreactive substituent. In **IV**, $X = Y = Cl$; $X = Cl, F$; $Y = NHR$ when $Z = N$ or $X = Y = Cl, F$ when $Z = C{-}Cl$, $n = 1$–6.

type of heterobifunctional dye, the two reactive groups are on the same side of the chromogen, while in **II**, designated a 'separated' type of heterobifunctional dye, they are on opposite sides. **III** is a vinylsulphone type of monofunctional dye which reacts by a nucleophilic addition mechanism and where there is frequently an elimination step before the addition step. **IV** is an *N*-heterocyclic type of mono- or bifunctional dye which reacts by an SN2 mechanism. **III** and **IV** include the most widely used reactive dyes for cellulose, i.e. VS and MCT dyes.

Compared with many types of reactive dye, **III** is characterized by excellent washing-off and acid-hydrolysis properties arising mainly from the properties of the VS group (Table 1); it is suitable for middle-temperature dyeing.[6] However, **III** is usually inferior to **IV** in some application properties, and also has a synthetic disadvantage in that the VS group must usually be synthesized as a substituent on an intermediate compound which is then used in dye preparation.[7] Attempts to introduce it directly into a particular position of a chromogen have been unsuccessful, owing to unsatisfactory selectivity and unavoidable side reactions and decompositions. More readily prepared are non-chromogenic, relatively simple compounds such as β-(sulphatoethylsulphonyl)anilines and these are used exclusively as building blocks of VS dyes. This synthetic requirement therefore severely restricts the degree of flexibility in designing dye structures, compared with the *N*-heterocyclic approach where the reactive group can simply be attached to any chosen chromogen having an amino group. In contrast to **III**, many chromogens are available for the preparation of **IV**, resulting in greater flexibility in molecular engineering techniques for the design of **IV**.

Therefore, the requirements for the design of heterobifunctional dyes to gain the best features of both **III** and **IV** are as follows:

(1) an amino-containing chromogen should be utilized, achieving the advantages of **IV**;
(2) a VS group should be selected as one of two reactive groups, achieving the advantages of **III**; and
(3) an MCT group should be selected not only as another reactive group but also as a ready means of combining the VS group with the chromogen through bridge links.

An MCT group is selected because of its economic attractiveness and the wider synthetic potential arising from the use of cyanuric chloride as a lower-priced starting material, compared with the other *N*-heterocyclic reactive systems. Initial considerations lead to **I** as being the most rational skeleton for heterobifunctional dyes, since any approach to **II** suffers from the same synthetic disadvantages noted above for **III**.

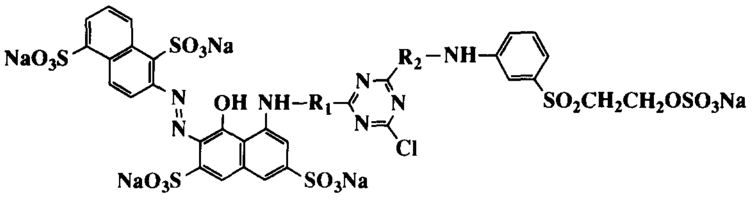
2.2 Optimization of VS/MCT reactive system

In the next stage of the design process, it was necessary to take account of the behaviour of **I** in its migration from a dyebath into the interior of cellulose and the fastness properties of the resulting dyed cellulose. To optimize the structure of **I**, the role of the two bridge links in dye performances was examined using dyes **1–5** (Table 2). These dyes are characterized by the chromogen producing a brilliant red colour; the *m*-phenyleneimino unit linked to the VS group originates from the use of 3-(β-hydroxyethylsulphonyl)aniline as a key intermediate. Figures 2 and 3 show the reaction sequences for dyes **2–4** and **5**, respectively. Dye **1** was prepared similarly using 3-(β-sulphatoethylsulphonyl)aniline in place of **11** (Fig. 2).

The dyeing behaviour of dyes **1–5** was followed spectrophotometrically and chromatographically by analysing aliquots taken at intervals from the dyebath. Just before alkali addition, dye **1** was 40% exhausted, almost retaining an ester form. Then, on adding alkali, it was converted readily into the vinyl form, with little accompanying hydrolysis of the MCT group. Subsequent reaction with cellulose led to 72% fixation, 14% (100% minus 86%) non-exhaustion and 14% (86% minus 72%) hydrolysis on cellulose. Dyes **2–5** were less substantive, resulting in lower fixation values (*FV*) (30–56%).

TABLE 2

Dyeing Properties in Relation to R_1 and R_2 of VS/MCT Dyes with a 1,5-Disulphonato-2-Napthylazo-H-Acid Chromogen



Dye no.	R_1[a]	R_2[a]	*EV (%)*[b]		*FV*[c] *(%)*	*Rel. FV*[d] *(%)*
			Primary	*Secondary*		
1	direct bond	direct bond	40	86	72	84
2	direct bond	$NHCH_2CO$	20	68	56	82
3	direct bond	$NHCH(CH_3)CO$	12	52	44	85
4	direct bond	$NHCH_2CH_2CO$	10	49	42	86
5	$COCH_2CH_2NH$	direct bond	9	35	30	86

[a] The NH in R_1 and R_2 is bonded to the triazine ring.

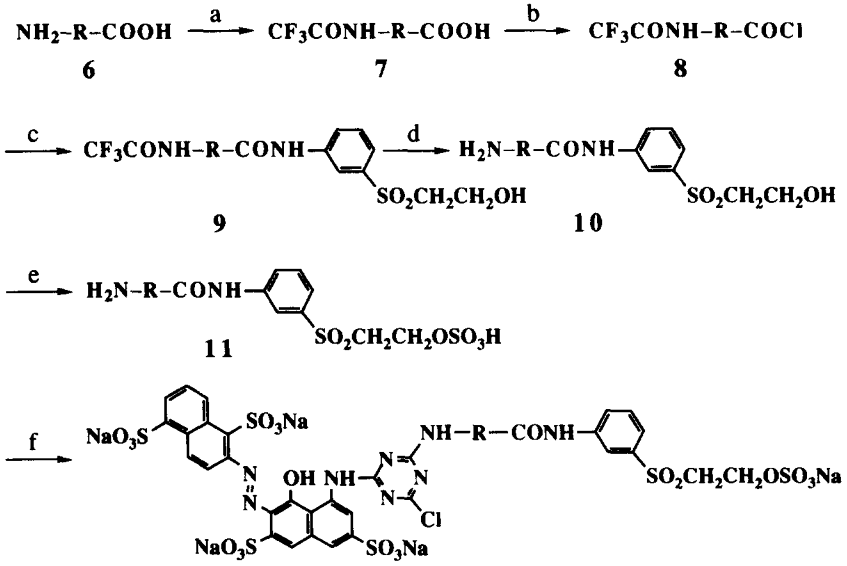
[b] Exhaustion value, which indicates portion of dye absorbed on (or fixed to) cellulose during a dyeing process. A primary *EV* means before alkali addition, and a secondary *EV* means after alkali addition.

[c] Fixation value, which indicates portion of dye forming one or two covalent bonds with cellulose.

[d] Relative fixation value, which indicates *FV*/secondary *EV*.

Considerable differences between the primary (before alkali addition) and secondary (after alkali addition) exhaustion values (*EV*) indicate that the β-sulphatoethylsulphonyl group not only behaves effectively as a temporarily water-solubilising group, but also plays a prominent role in giving a characteristic exhaustion–fixation profile similar to that generally observed for VS dyes. This relates to the observation that the reaction of VS/MCT dyes with cellulose proceeds primarily through the more reactive VS group. In contrast, for MCT dyes the difference is usually much smaller.[8] A VS/MCT dye is, therefore, clearly distinguished from an MCT dye in dyeing behaviour.

The most remarkable feature shown in Table 2 is that the fixation value (*FV*) is proportional to the secondary *EV* (*Rel. FV* = 82–86%), depending on the nature of the bridging groups R_1 and R_2. Thus, *FV* increases linearly with increasing secondary *EV*, provided that it is not too high; too high an *EV* is not advantageous for achieving high *FV* and level dyeing.[9,10] This finding indicates that the judicious selection of R_1 and



2 (R = CH_2); 3 (R = $CH(CH_3)$); 4 (R = CH_2CH_2)

Fig. 2. Reaction sequence used to prepare dyes 2–4. Reagents: (a) $(CF_3CO)_2O/CH_2Cl_2$; (b) $SOCl_2$; (c) 3-(β-hydroxyethylsulphonyl)aniline/acetone/pyridine; (d) K_2CO_3/CH_3OH-H_2O; (e) H_2SO_4/*N*-methylpyrrolidone; (f) tetrasodium 5-(2,4-dichloro-1,3,5-triazin-6-ylamino)-3-(1,5-disulphonato-2-naphthylazo)-4-hydroxynaphthalene-2,7-disulphonate/Na_2CO_3/H_2O.

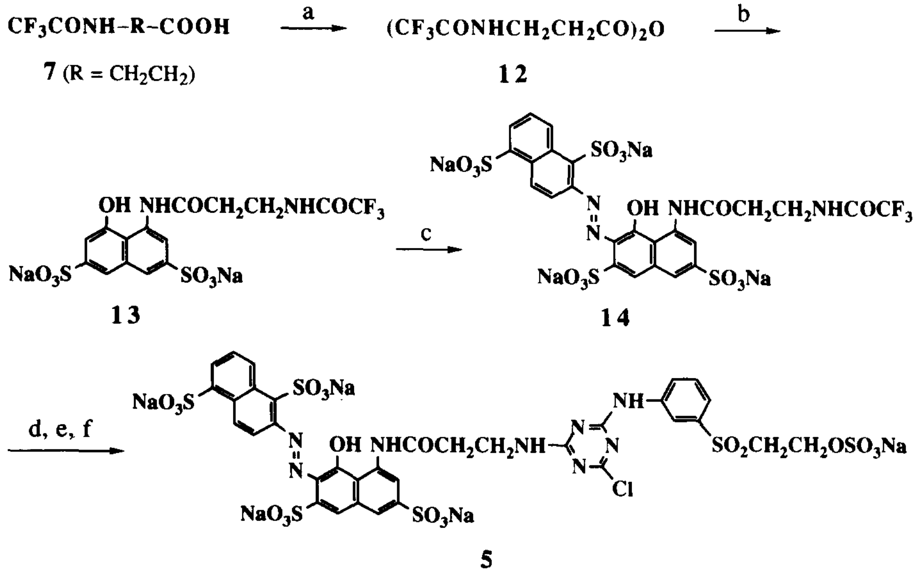
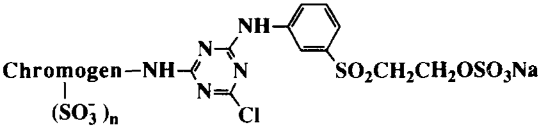


Fig. 3. Reaction sequence used to prepare dye 5. Reagents: (a) dicyclohexylcarbodiimide/CH_2Cl_2; (b) H-acid/Na_2CO_3/H_2O; (c) 2-diazonionaphthalene-1,5-disulphonic acid/Na_2CO_3/H_2O; (d) Na_2CO_3/H_2O; (e) cyanuric chloride/Na_2CO_3/H_2O; (f) 3-(β-sulphatoethylsulphonyl)-aniline/Na_2CO_3/H_2O.



V

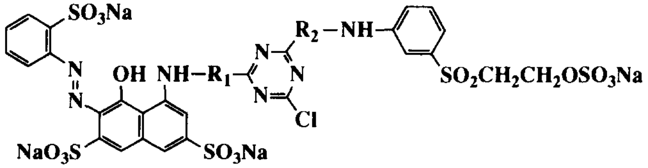
Fig. 4. Optimized structure of a VS/MCT reactive system, which leads to distinct advantages over mono- and homobifunctional reactive systems.

R_2 will result in adjustment to the secondary *EV*. In this series, since the increasing flexibility of R_1 and R_2 reduces the primary and the secondary *EV*, it is quite important to shorten their length so as to give rigidity to the bifunctional reactive unit. The optimized structure of **I** is shown in Fig. 4.

The validity of the formula for **V** has been confirmed by a further series of VS/MCT dyes having another chromogenic system (Table 3). The lower *EV*s and *FV*s can be ascribed to the different chromogenic system used, but evidence against this has been found in another series of dyes in which the *m*-phenyleneimino unit of dye **15** is systematically varied (Table 4). In isomeric phenyleneimino systems, the *EV* and *FV* are in the following decreasing order: $m \approx p \gg o$ (**15**, **18** and **19**). A similar effect holds for the substituents in *m*-(β-sulphatoethylsulphonyl)anilino dyes: *p*-OCH_3 (**21**) $\gg$ *o*-OCH_3 (**20**) > *N*-C_2H_5 (**22**). Thus, substituents adjacent or bonded to the imino nitrogen atom significantly change their *EV*s and *FV*s. The almost unchanged *Rel. FV*s suggest that a principle determining factor is the substantivity of the dyes. Since such substituents decrease the coplanarity of the

TABLE 3

Dyeing Properties in Relation to R_1 and R_2 for VS/MCT Dyes with a 2-Sulphonatophenyl-Azo-H-Acid Chromogen



Dye no.	R_1[a]	R_2[a]	*EV (%)*		*FV (%)*	*Rel. FV (%)*
			Primary	*Secondary*		
15	direct bond	direct bond	20	63	50	79
16	direct bond	$NHCH_2CH_2CO$	8	35	27	77
17	$COCH_2CH_2NH$	direct bond	4	22	17	77

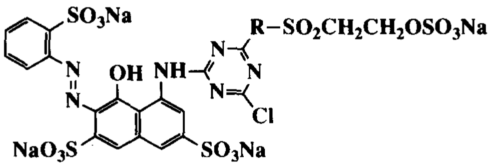
[a] The NH in R_1 and R_2 is bonded to the triazine ring.

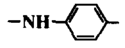
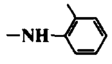
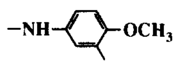
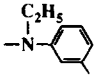
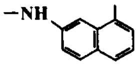
anilinotriazinyl ring system,[11] the apparent explanation for this substituent effect is that the substantivity is reduced by nonplanar conformational distortion of the bifunctional reactive unit arising from substituent crowding at the periphery of the imino nitrogen atom. The larger naphthyleneimino in dye **23** markedly increased the *EV*, but decreased the *FV* owing to its poor diffusibility (lower *Rel. FV* of 49%). The more flexible ethyleneimino in dye **24** reduced the *EV* and decreased the *FV*. Therefore, the configuration, ring size and flexibility of the bridge link are all influential factors to be considered when optimizing the VS/MCT reactive system.

2.3 Dyeing properties of VS/MCT dyes

Temperature-insensitive reactive dyes have recently become of interest, since the *FV*s of conventional reactive dyes often fluctuate owing to the

TABLE 4
Relationships between Bridge Link *R* and Dyeing Properties



Dye no.	*R*[a]	*EV (%)*		*FV (%)*	*Rel. FV (%)*
		Primary	*Secondary*		
18		18	67	51	76
19		10	41	32	78
20		18	42	33	79
21		25	67	50	75
22		8	36	28	78
23		50	80	39	49
24	$-NHCH_2CH_2-$	8	48	40	83

[a] The nitrogen atom in *R* is bonded to the triazine ring.

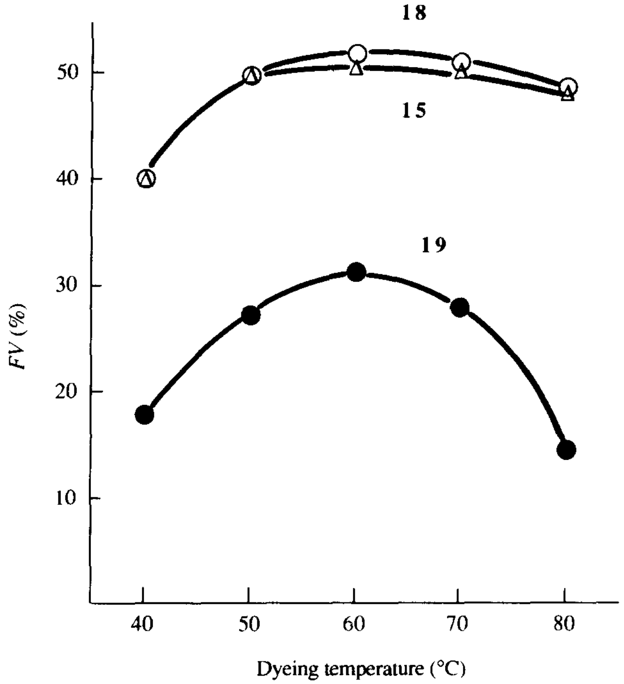


Fig. 5. Temperature dependence of fixation for isomeric dyes **15**, **18** and **19**.

non-uniformity of temperature distribution in a dyebath.[1] Figure 5 shows the temperature dependence of fixation for dyes **15**, **18** and **19**, observed under exhaust dyeing conditions between 40 and 80°C. The *m*- (**15**) and *p*-isomers (**18**) are characteristically insensitive to temperatures of 50–80°C, having FV_{min}/FV_{max} values (Δf) of 0.95 and 0.94, respectively; the dyes gave nearly equal colour depth to each of the dyeings. In contrast, the *o*-isomer (**19**) is very sensitive (Δf = 0.45), its sensitivity being similar to that of VS dyes. Accordingly, VS/MCT dyes are not always insensitive to temperature, although it has been believed that the synergism of both reactive groups in the same molecule leads to temperature-insensitivity, with low temperatures favouring the more reactive VS group and with high temperatures increasing the possibility of reaction of the less reactive MCT group in a fixation process.[1]

Other temperature-sensitive VS/MCT dyes are exemplified in Fig. 6. Dyes **22** and **25** behave like a VS dye, having relatively sharp temperature–fixation curves through a maximum at 50°C (Δf = 0.62 and 0.33, respectively). Dye **23** behaves like an MCT dye, having the curve sloping to the right (Δf = 0.51). It is evident that not only the two reactive groups, but also their bridge link, affect the temperature dependence, and that both steric and positional effects are involved. The importance of the steric

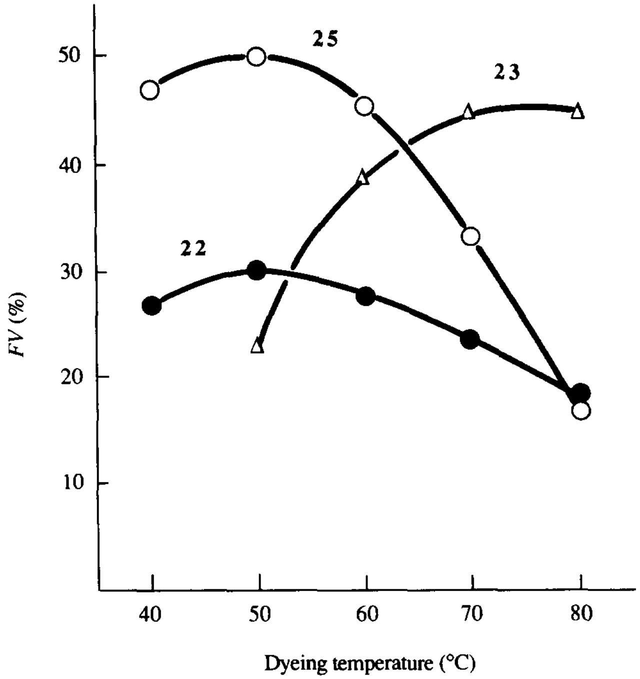
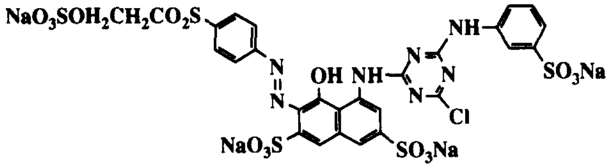


Fig. 6. Temperature dependence of fixation for dyes having an *N*-ethyl-*m*-phenyleneimino (**22**), a 1,7-naphthyleneimino (**23**) and a separated type of heterobifunctional system (**25**). Its chemical structure is as follows:



25

effect is evident from the increase in temperature sensitivity produced by virtually all substituents adjacent to or bonded to the imino nitrogen atom.

In reactive dyeing, fixation is a function of reactivity, substantivity and diffusibility under a given dyeing condition,[5] and each of these is also a function of temperature. Thus, the temperature dependence of fixation for a VS/MCT dye can be explained in terms of the complementary behaviour of these factors for temperature variations. Increasing diffusibility of the dye and increasing reactivity of its MCT group with increasing temperature increases the *FV*; in contrast, decreasing substantivity of the dye and increasing hydrolysis of its VS group decreases the *FV*. With lowering of temperature, each factor acts in the reverse manner. When the structure of the dye is designed in such a way that the temperature effects on these influential factors tend to compensate for each other, the *FV* will become independent of temperature variations.

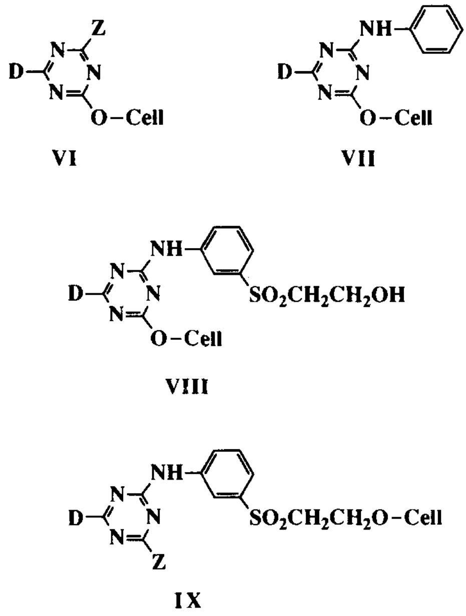
In the dyes examined, the temperature effect on the reactivity for each of the two reactive groups should be the same; substantivity and diffusibility will become the dominant factors determining the temperature dependence of fixation. Since increasing the substantivity tends to be incompatible with increasing the diffusibility, this leads to difficulties in the design of high fixation dyes, but fortunately is convenient in the design of temperature-insensitive dyes. From these considerations, judicious selection of *R* in the structure shown in Table 4 makes it possible to reveal temperature-insensitive dyeing behaviour. Both the *N*-ethyl-*m*-phenyleneimino group (in **22**), which imparts low substantivity and probably good diffusibility, and the 1,7-naphthyleneimino group (in **23**), which imparts high substantivity and poor diffusibility, are unsuitable for *R*. More suitable are the *m*- and *p*-phenyleneimino groups (in **15** and **18**, respectively), which impart both moderate substantivity and moderate diffusibility.

Temperature-insensitive dyes can be developed based on compound **V**, some of which have been disclosed in the patent literature.[12,13] A very wide range of optimal dyeing temperatures is an industrially important feature, because the temperature distribution in a dyebath is prone to non-uniformity, particularly during winch dyeing; this results in dyeings with excellent shade reproducibility and levelness factors, which are necessary in attaining 'right-first-time' production processes.

2.4 Fastness properties of VS/MCT dyes

VS/MCT reactive dyeings result from the very complex competitive system of fixation reaction versus hydrolysis.[14] If a VS/MCT dye is bound to cellulose by the more reactive VS group, the less reactive MCT group can also react with it, forming **IX**(Z = O–Cell) (Fig. 7) or, if this is impossible for steric reasons, it remains unchanged as it in **IX**(Z = Cl) or is hydrolysed to form **IX**(Z = OH). Even if either of the two groups is hydrolysed before being bonded to cellulose, another group can be bound to it leading to **VIII** and **IX**(Z = OH). Thus, the four fixation modes are present in the VS/MCT reactive dyeing. This has been supported by enzymatic degradation studies on cotton dyeings from a separated type of VS/MCT dye.[15]

The temperature-insensitive fixation observed in the VS/MCT reactive dyeing suggests that the proportion of the four fixation modes depends on dyeing temperature. Accordingly, another important aspect is the fastness properties. It is important from a practical point of view to



VI VII VIII IX

Fig. 7. Schematic chemical structures of dyes fixed to cellulose (HO–Cell). **VI** and **VII** are from a DCT and an MCT dye, respectively. VS/MCT dye **V** (Fig. 4) gives **VIII** and **IX**, depending on whether either or both of the MCT and VS groups react with cellulose or water, *Z* is chloro, hydroxy or O–Cell. *D* is a chromogenic part.

examine whether the fastness properties are affected by the fixation modes or not. Three analogues of dye **15**, having a β-hydroxyethylsulphonyl group in place of the β-sulphonatoethylsulphonyl group, and a hydroxy and a methoxy group in place of the chloro group, were synthesized and allowed to react with cellulose to obtain **VIII**, **IX**(Z = OH) and **IX**(Z = OCH_3), respectively, in which D is a 2-sulphonatophenylazo-H-acid moiety. Because of the difficulty in the selective preparation of **IX**(Z = O–Cell), a structurally simpler analogue (**IX**(Z = OCH_3)) was used. In the preparation of **IX**(Z = Cl), the reaction of the chloro group with water and cellulose was unavoidable; the dyeings from dye **15** were therefore used, containing a concentration of 30±10% against the mole of the total fixed dyes.

Table 5 shows their fastness properties and those of comparable dyeings from a DCT (dichlorotriazinyl) and an MCT dye with the same chromogenic system (**VI** and **VII**, respectively). All fastness properties are independent of the fixation modes, the only exception being the fastness to acid hydrolysis. In particular, wool staining in this test is clearly dependent on the fixation mode, suggesting that the triazinyl–cellulose bonds in **VI** and **VII** are less stable under acid conditions than the sulphonylethyl–

TABLE 5
Fastness Properties of **VI–X** Having a 2-Sulphonatophenylazo-H-Acid Chromogen

No.	*Light*	*Perspiration–light*		*Chlorinated water*	*Wash*[a]			*Acid hydrolysis*[a]		
		Acid	*Alkaline*		*cc*	*c*	*w*	*cc*	*c*	*w*
VI[b]	5	3–4	3	4	5	4–5	4	4–5	3	1–2
VII	5	3–4	3	4	5	4–5	4	5	4–5	2
VIII	5	3–4	3	4	5	4–5	5	5	4–5	3
IX (Z = OH)	5	3–4	3	4	5	4–5	5	5	4–5	3–4
IX (Z = OCH_3)	5	3–4	3	4	5	4–5	5	5	5	3–4
X[c]	5	3–4	3	4	5	4–5	5	5	5	3–4

[a] cc: colour change, c: cotton staining, w: wool staining.
[b] Dyeings from the DCT dye, which comprised **VI** (Z = Cl, OH and O–Cell).
[c] Dyeings from dye **15**, which comprised **VIII** and **IX** (Z = Cl, OH and O–Cell).

cellulose bonds in **IX**(Z = OH and OCH_3), although the bond in **VIII** is slightly less stable. This tendency is consistent with those for DCT, MCT and VS dyes.[16,17] Since the staining of the adjacent wool was deeper than that of the adjacent cotton, the dyebases liberated by the cleavage of the dye–cellulose bonds are less substantive to the cotton, being hardly able to redye it, but they can redye the wool considerably because of the different dyeing process promoted by an ionic-bonding mechanism. The colour changes of all dyeings tested (4–5 or 5 grade) show that the dyebases are present in very small amounts, particularly in **VII–X**.

The wool staining observed in **VIII** was unobservable in **X** containing it. Therefore, it is concluded that the fastness properties of dyeings from **15**, such as light, perspiration–light, chlorinated water and wash fastness, are independent of the proportions of the four fixation modes. The resulting great advantage to practical dyeing is that such well-designed VS/MCT dyes give dyeings having fastness properties which are independent of dyeing temperature. This also makes it possible to assess the fastness properties of VS/MCT dyes exactly, using the dyeings obtained at a particular dyeing temperature.

Table 6 shows the fastness properties of the dyeings obtained at 60°C for all VS/MCT dyes examined. With a few exceptions, only under acid-hydrolysis conditions does the wool staining depend on the bifunctional systems. Small differences in perspiration–light and chlorinated water fastness between dyes **1–5** and **15–24** are due to differences in the chromogens used.[18] The anomalous chlorinated water fastness of dye **21** is due to the powerful electron-donation of the p-OCH_3 group. These results also support the validity of the formula of compound **V**.

TABLE 6
Fastness Properties for VS/MCT Dyes

Dye no.	*Light*	*Perspiration–light*		*Chlorinated water*	*Wash*[a]			*Acid hydrolysis*[a]		
		Acid	*Alkaline*		*cc*	*c*	*w*	*cc*	*c*	*w*
1	5	3	2–3	4–5	5	4–5	5	4–5	4–5	3–4
2	5	3	2–3	4	5	4–5	5	4–5	4–5	3
3	5	3	2–3	4–5	5	4–5	5	4–5	4–5	3
4	5	3–4	2–3	4–5	5	4–5	5	4–5	4–5	3–4
5	5	3	2–3	4–5	5	4–5	5	4–5	4–5	2
15	5	3–4	3	4	5	4–5	5	5	5	3–4
16	5	3	3	3–4	5	4–5	5	4–5	4–5	4
17	5	3	3	4	5	4–5	5	4–5	3–4	2
18	5	3–4	3	4	5	4–5	5	5	5	2
19	5	3–4	3	4	5	4–5	5	5	4	2
20	5	3	3	4	5	4–5	5	5	5	3
21	5	3–4	3	2–3	5	4–5	5	5	5	3
22	5	3–4	3	4	5	4–5	5	5	5	3–4
23	5	3–4	3	4	5	3	4–5	4–5	4	3
24	5	3–4	3	4	5	4–5	5	5	5	4

[a] cc: colour change, c: cotton staining, w: wool staining.

2.5 Colour change of VS/MCT reactive dyeings by amine

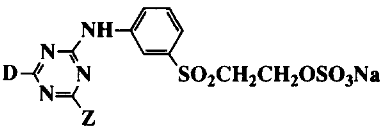
Potentiometric titration with $AgNO_3$ showed that the content of component **IX**(Z = Cl) in the dyeings from dye **15**, which was dyed at 60°C, was 30±10% in concentration against the mole of the total fixed dyes; for dye **27** (Table 7) the content is 90–100% under the same dyeing conditions. For a separated type of VS/MCT dye with a twice-coupled H-acid chromogen, the content has been reported to be 25±12%.[15] These results indicate that the reactivities of these MCT groups depend strongly on the chromogens used.

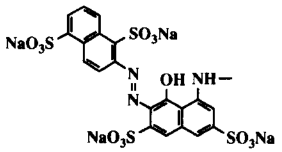
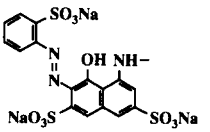
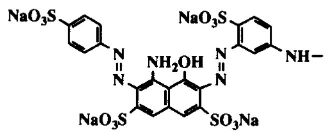
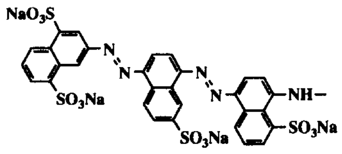
The remaining MCT group has lower reactivity, but can react with amines at elevated temperatures when the dyeings are treated with amine-containing dye-fixing agents. This treatment has often been used for improving the wash fastness of the dyeings in which unfixed (hydrolysed) dyes remain, and, as a result, for shortening the washing-off process.[19]

Table 7 shows that the colour change of VS/MCT reactive dyeings caused by the fixation treatment is very small for the hydroxyazo dyes **1**, **15** and **26** (4–5 grade), and is very pronounced for the aminoazo dye **27** (1 grade). The shifts in λ_{max} of the dyes with changes in Z from chloro to morpholino explain these colour changes. The large bathochromic

TABLE 7

Colour Changes of VS/MCT Dyes by Morpholino Substituent in Aqueous Solutions and Those of Their Dyeings by Fix Treatment



Dye no. (Z = Cl)	*D*	*λ_{max} (nm) when Z =*		*Colour change of dyeings by fix treatment*
		Cl	*Morpholino*	
1		518 543	522 543	4
15		514 534	518 534	4–5
26		599	600	5
27		487	510	1

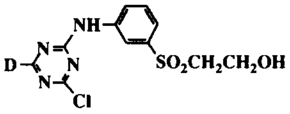
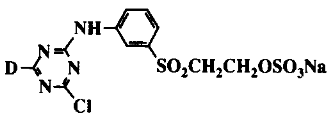
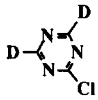
shift (23 nm) of dye **27** can be related to the fact that the position of the aminoazo–iminohydrazone tautomeric equilibrium of aminoazo dyes is susceptible to substituents on the amino group, resulting in significant shifts of the λ_{max}.[20] Therefore, attention should be called to the design of VS/MCT dyes with such aminoazo chromogens.

2.6 Possibility of polyfunctional dyes

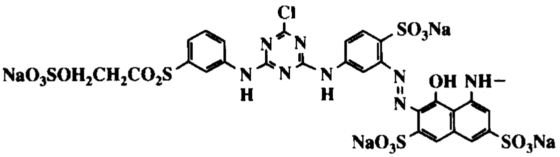
Table 8 shows that not all polyfunctional dyes have high *FV*s. In particular, the *FV* value for dye **30** (which is about twice the size of a normal red VS/MCT dye and has five independent reactive groups in the same

TABLE 8

Effect of Polyfunctionality on *FV*

Dye no.	*Structure*[a]	*Number of reactive groups*	*FV (%)*
28		1VS 2MCT	36
29		2VS 2MCT	56
30		2VS 3MCT	30

[a] *D* is as follows:



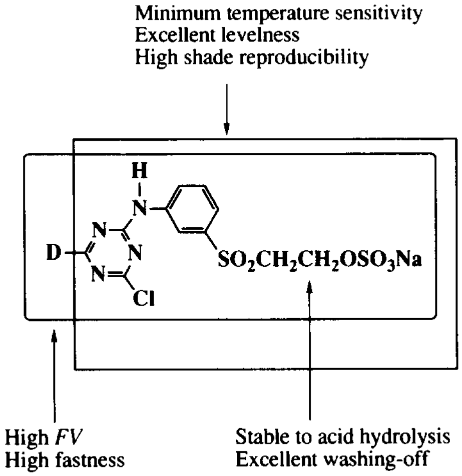


Fig. 8. Relationships between the technically important application properties and their relatable structural units for optimized VS/MCT dyes.

molecule) is very low, regardless of the increased substantivity and greater possibilities of fixation. This indicates the importance of diffusibility. VS/MCT dyes which have both a not too high substantivity and a moderate diffusibility are suitable for high-fixation dyeing.

Figure 8 summarizes the relationships between the technically important application properties and their related structural units for optimized VS/MCT dyes.

3 EXPERIMENTAL

3.1 Materials

First-grade or technical-grade reagents were used for the syntheses. Special-grade reagents or their equivalent, and water purified by ion exchange, were used for analysis, dyeing and fastness tests. Scoured and bleached unmercerized cotton knitted fabrics for dyeing were obtained from Nitto Boseki Co. Ltd.

3.2 Measurements

Visible absorption spectra were recorded on a Hitachi UV/Visible spectrophotometer model 228A, using water as solvent, unless otherwise noted. HPLC analyses were performed with a Shimadzu model LC-3A liquid chromatograph with a 4.0 mm (i.d.) × 250 mm Lichrosorb RP-18 column (Merck, reverse phase, 5 μm), using methanolic water solutions as eluent.

3.3 Syntheses

Dyes **1**, **15** and **18–30** were synthesized following the previously reported methods.[12,21–23] Dyes having a morpholino group in place of the chloro group in dyes **1**, **15**, **26** and **27** were synthesized by reacting morpholine with these dyes.

Dye **4** was synthesized as follows: trifluoroacetic anhydride (81.0 g, 386 mmol) was added dropwise to β-alanine (31.2 g, 350 mmol) in CH_2Cl_2 (300 ml) over a period of 1 h with external ice cooling, and the mixture was then stirred at 20–30°C for 2 h. After evaporation of the reaction mixture, the resulting oily residue was redissolved in AcOEt. The solution was washed with water and dried over Na_2SO_4. Evaporation of the solvent afforded colorless crystals of **7** (R = CH_2CH_2) (62.2 g, 336 mmol, 96%). The product (30.0 g, 162 mmol) was added to $SOCl_2$ (38.5 g, 324 mmol) over a period of 1 h at 20–30°C, and stirring was continued for 3 h at 30–40°C. The reaction mixture was concentrated under reduced pressure to afford a colorless oil (33.3 g, c. 100%). This was immediately dissolved in toluene (20 ml) and the solution added dropwise to a solution of 3-(β-hydroxyethylsulphonyl)aniline (32.5 g, 162 mmol) and pyridine (12.0 g, 162 mmol) in acetone (150 ml) (ice bath). The mixture was stirred overnight at 20–30°C, then the product was extracted with AcOEt, washed with water and dried over Na_2SO_4. Evaporation of the solvent gave pale brown crystals of **9** (53.3 g, 145 mmol, 89%). The analysis was as follows. Calculated for $C_{13}H_{15}N_2O_5SF_3$: C, 42.51; H, 4.09; N, 7.63. Found: C, 42.46; H, 4.47; N, 7.74.

Mass spectrometric analysis was satisfactory for **9**. Hydrolysis and esterification afforded **11**, and finally condensation with tetrasodium 5-(2,4-dichloro-1,3,5-triazin-6-ylamino)-3-(1,5-disulphonato-2-naphthylazo)-4-hydroxynaphthalene-2,7-disulphonate gave dye **4**. Dyes **2**, **3**, **5**, **16** and **17** were synthesized similarly. All dyes were purified by repeated recrystallization until chromatographically pure.

3.4 Dyeing

Each solution (200 ml) was prepared at 20–30°C with dye, Na_2SO_4 (10.0 g) and water, in which the dye concentration was 5.62×10^{-4} mol dm^{-3} for dyes **1–5** and 8.23×10^{-4} mol dm^{-3} for dyes **15–24** and **28–30**. The temperature of each dyebath was raised to 60°C, and cotton (10.0 g) was immersed in the dyebath for 20 min with stirring to permit primary exhaustion. Na_2CO_3 (4.0 g) was then added and dyeing was continued for a further 60 min at 60°C to permit secondary exhaustion. After dyeing, the cotton was rinsed with cold water and then boiling water to remove unfixed (hydrolysed) dye, and dried.

3.5 Exhaustion value (*EV*) and fixation value (*FV*)

Measurements were made spectrophotometrically on the residual dyebath solutions after primary and secondary exhaustion, and on the solutions prepared by dissolving the dyed cotton in 70% H_2SO_4, to determine the primary and secondary *EV*s and *FV*s, respectively, all of which were based on the amount of dye used.

3.6 Temperature dependence

The dyeing in Section 3.4 was repeated using dyes **15**, **18**, **19**, **22**, **23** and **25**, but at dyebath temperatures of 40, 50, 70 and 80°C instead of 60°C.

The *FV*s determined gave the temperature–fixation curves in the range 40–80°C.

3.7 Fastness

Dye **1–5**, **16–24**, **26** and **27** were dyed following the same method as in Section 3.4, except for varying the amount of each dye used so as to give nearly equal colour depth to the dyeings obtained from dye **15**. **VI–VIII**, **IX**(Z = OH) and **IX**(Z = OCH_3) having a 2-sulphonatophenylazo-H-acid chromogen were prepared from the corresponding reactive dyes under the same dyeing conditions, except that the dyeing was performed at 30°C for **VI** and 80°C for **VII**. For all dyeings, light, perspiration–light, chlorinated water and wash fastness tests were carried out according to JIS L 0842 (method 2), JIS L 0888 (method B), ISO 105–E03 and JIS L 0844 (method A–4), respectively. Acid-hydrolysis fastness was tested by immersing each dyeing in 1% AcOH for 30 min, and treating on a perspirometer at 37±2°C for 6 h under 125 g cm^{-2}. The results were assessed in ratings from grade 1 (very poor) to grade 8 (excellent) for the light fastness test, and from grade 1 (poor) to grade 5 (excellent) for the other tests.

3.8 Colour change of dyeings by fix treatment

The test was carried out for each dyeing from dyes **1**, **15**, **26** and **27** obtained in Section 3.7. A drop of Danfix 505RE (quaternary ammonium-type cationic polymer, Nitto Boseki Co.) was spotted onto each dyeing. It was then immersed in hot water (60–70°C) for 20 min and dried. The colour change was assessed against the grey scale for colour change, ratings being from grade 1 (much altered) to grade 5 (unaltered).

CONCLUSIONS

The presence of two different reactive groups in the same molecule is shown to markedly improve the application properties of certain dyes compared with mono- and homobifunctional dyes. From this initial finding, a wide range of possibilities is thus opened up for the development of new heterobifunctional dyes. Well-designed VS/MCT dyes with satisfactory application properties are created not only by combination of both reactive groups with a chromogen, but also by judicious selection of the bridge links connecting these units. Such VS/MCT dyes offer a number of distinct advantages over comparable VS or MCT dyes.

ACKNOWLEDGEMENTS

We are indebted to Mr M. Sunami and Dr N. Harada for their cooperation in this project.

REFERENCES

1. Fujioka, S. & Abeta, S., *Dyes and Pigments*, **3** (1982) 281.
2. Siegel, E., In *The Chemistry of Synthetic Dyes, Reactive Dyes.* ed. K. Venkataraman. Academic Press, New York, 1972, Vol. 6, pp. 195–200.
3. Renfrew, A. H. M. & Taylor, J. A., *Rev. Prog. Coloration*, **20** (1990) 1.
4. Zollinger, H., In *Color Chemistry.* VCH, Weinheim, 1991, pp. 178–9.
5. Sumner, H. H. & Vickerstaff, T., *Melliand Textilber.*, **42** (1961) 1161.
6. Abeta, S., Yoshida, T. & Imada, K., *Am. Dyest. Rep.*, **73** (July 1984) 26.
7. Beech, W. F., In *Fibre-Reactive Dyes.* Logos, London, 1970, p. 212.
8. Bradbury, M. J., Collishaw, P. S. & Phillips, D. A. S., *J. Soc. Dyers Colour.*, **108** (1992) 430.
9. Vickerstaff, T., *J. Soc. Dyers Colour.*, **73** (1957) 237.
10. Ramsay, D. W., *J. Soc. Dyers Colour.*, **97** (1981) 102.
11. Abeta, S., Akahori, K., Meyer, U. & Zollinger, H., *J. Soc. Dyers Colour.*, **107** (1991) 12.
12. Omura, T., Tezuka, Y., Sunami, M. & Sumitomo Chemical, *US Patent* 4 412 948 (1983).
13. Morimitsu, T., Kikkawa, S., Omura, T. & Sumitomo Chemical, *US Patent* 4 837 310 (1989).
14. Matsui, M., Meyer, U. & Zollinger, H., *J. Soc. Dyers Colour.*, **104** (1988) 425.
15. Meyer, U., Müller, S. & Rys, P., *Textilveredlung*, **26** (1991) 80.
16. Senn. R. C. & Zollinger, H., *Helv. Chim. Acta*, **46** (1963) 781.
17. Senn, R. C., Stamm, O. A. & Zollinger, H., *Melliand Textilber.*, **44** (1963) 261.
18. Omura, T., Kayane, Y. & Tezuka, Y., *Dyes and Pigments*, **20** (1992) 227.
19. Kaneko, T., *Senshoku Kogyo*, **39** (1991) 536.
20. Omura, T., *Dyes and Pigments*, **23** (1993) 179.
21. Tezuka, Y., Sunami, M., Omura, T., Kayane, Y. & Sumitomo Chemical, *US Patent* 4 341 699 (1982).
22. Omura, T., Sunami, M., Tezuka, Y. & Sumitomo Chemical, *US Patent* 4 663 440 (1987).
23. Morimitsu, T., Harada, N., Omura, T., Kikkawa, S. & Sumitomo Chemical, *US Patent* 5 116 959 (1992).